# EFFECT OF COUNTER ION VALENCY ON DYNAMICS OF SODIUM SULFONATED POLYSTYRENE

*A Thesis submitted*

*by*

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*In partial fulfilment of the award of the degree of*

*Master of Science*

*Under the academic autonomy*

**National Institute of Technology, Rourkela**

*Under the guidance of*

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# DECLARATION

I hereby declare that the work carried out in this thesis is entirely original. It was carried out at the Department of Physics and Astronomy, National Institute of Technology, Rourkela. I further declare that it has not formed the basis for the award of any degree, diploma or similar title of any university or institution.

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# CERTIFICATE

This is to certify that the thesis entitled **"EFFECT OF COUNTER ION VALENCY ON DYNAMICS OF SODIUM SULFONATED POLYSTYRENE"** is a bonafide work of Ms. Sagarika Swain, in partial fulfilment of the requirements for the award of the degree of Master of Science in Physics at National Institute of Technology, Rourkela carried out by her under my supervision. To the best of my knowledge, the experimental matter embodied in the thesis has not been submitted to any other University/Institute for the award of any degree or diploma.

**Date: 10th May 2014**

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## ABSTRACT

We have studied the effect of counter ion valency on the chain dynamics of sodium sulfonated polystyrene polyelectrolyte having molecular weight, 1000 kDa. We have investigated the chain conformations as a function of counter ion valency and salt concentration using Dynamic Light Scattering. In the absence of added salt the polyelectrolyte assumes an extended structure. With addition of salt the hydrodynamic radius of the polyelectrolyte decreases on account of the screening effect of the added salt ions that effectively reduces the electrostatic repulsion between the like charged monomer units. With increase in ionic strength the polyelectrolyte chain acquires a coil like conformation. Reduction in size of the chain in presence salts having higher valency occurs at a much lower salt concentration as compared to monovalent salts.

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# CHAPTER – 1

# INTRODUCTION

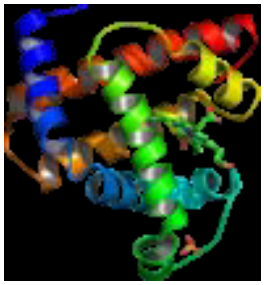
## 1.1 POLYMERS

Polymers are compounds with high molecular weight formed by the process of polymerization of smaller structural units known as the "monomers". The properties of polymer depend on the chemical composition of its monomer, degree of polymerization N and its architecture [1]. Some of the common examples are DNA, RNA, glucose, wood, propane, paraffin wax, proteins, vinyl chloride, sodium sulfonated polystyrene, nylon, polyethylene etc.

**Propane**

**Paraffin wax**

**DNA**



**Proteins**

**Nylon**

**Wood**

**Polyethylene**

**Figure 1 Examples of different polymers**

## 1.2 ELECTROLYTES

Electrolytes are compounds which ionize on being dissolved in polar solvents producing an electrically conductive medium. Commonly known examples of electrolytes are simple salts like metal chlorides, sulpahtes, phosphates etc. The ionization of electrolytes is represented by the following general equation,

$$MX(s) \rightarrow M^{+}\,(aq.) + X^{-}\,(aq.)$$

A specific example of such ionization is the dissociation of sodium chloride (NaCl) with $Na^{+}$ and $Cl^{-}$ ions.

$$NaCl(s) \rightarrow Na^{+}\,(aq.) + Cl^{-}\,(aq.)$$

## 1.3 POLYELECTROLYTES AND THEIR CLASSIFICATION

Apart from polymers and electrolytes which exhibit a completely distinct set of solution properties there exists a class of compounds which exhibit properties similar to both [2]. This class of compounds are better known as the "Polyelectrolytes". Polyelectrolytes have high molecular weight similar to that of the polymers and also get ionized thus exhibiting electrolytic behaviour. These polymers develop a substantial amount of charges on their backbone when dissolved in polar solvents by dissociating into polyions and associated counter ions. The counter ions carrying opposite charges to that of the polyions are always associated with the chain backbone keeping the overall system neutral. The number of counter ions is also an estimate of number of charged monomeric units on the polymer chains. A simple expression depicting the polyelectrolytic behaviour is given by:

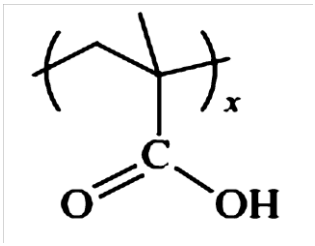
$$\boldsymbol{Polyelectrolyte}\ (\boldsymbol{s}) \xrightarrow{\boldsymbol{in\ polar\ medium}} \boldsymbol{Charged\ polymer\ chains + Counterions}$$

Some examples of such charged polymers are polyacrylic acid (PAA), polymethacrylic acid (PMAA) and their salts, sodium and Calcium salts of poly styrene sulfonic acid, polyvinyl sulphate, deoxyribonucleic acid (DNA), ribonucleic acid (RNA), proteins etc.

The choice of polyelectrolytes for a certain application depends on its nature and type of charge it carries. Polyelectrolytes are broadly classified as the natural, synthetic or chemically modified depending on the source from which they are obtained.

- Natural and Synthetic polyelectrolytes

Natural polyelectrolytes form a major component of nucleus of living cells like deoxyribose nucleic acid (DNA) which plays a vital role in the transfer of genetic materials, and ribonucleic acid (RNA). Proteins are yet another group of substances which have polyelectrolytic character which play a significant role in the smooth functioning of the life itself. Synthetic polyelectrolytes are synthesized by polymerization of charged monomer, or by modification of neutral polymers [2]. Some of the synthetic polyelectrolytes are poly (acrylic acid), poly (2-vinyl-pyridine), poly (methacrylic acid) and salts of poly(styrene sulfonic acid).




**(a) DNA** **(b) Polymethacrylic acid**

**Figure 2 (a) Natural polyelectrolyte, (b) Synthetic polyelectrolyte**

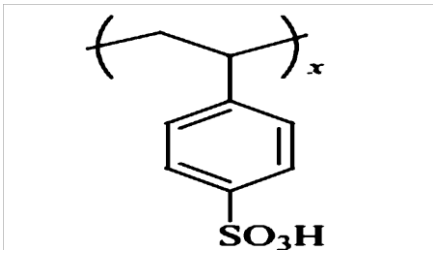
- Anionic and Cationic Polyelectrolytes

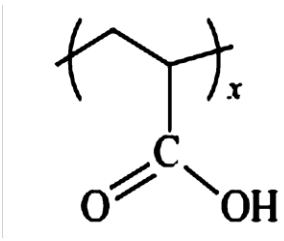
Further the polyelectrolyte can be classified as anionic or cationic depending on the charges it acquires at its backbone upon dissociation. If after the dissociation, polyelectrolyte acquires negative charges then it is termed as anionic while cationic polyelectrolyte acquires positive charges on their backbone. The anionic groups generally include sulfate, phosphate, sulfonate, and carboxyl, while that of cationic groups includes protonated ammonium, quaternized ammonium, sulfonium, and phosphonium [2].

- Strong and Weak polyelectrolytes

Based on the degree of dissociation the polyelectrolytes can be classified as strong or weak polyelectrolytes. Strong polyelectrolytes exhibit a complete dissociation for a wide range of solution. Examples of polymers exhibiting strong polyelectrolytic nature are sodium sulfonated polystyrene (NaPSS) and polydiallyldimethylammonium chloride (PDADMAC).

In contrast to their strong counterpart, weak polyelectrolytes .show a strong dependence on solution pH. For example Polyacrylic acid, poly allylamine hydrochloride exhibit weak polyelectrolytic nature.




**(a) Poly (styrene sulfonate)** **(b) Polyacrylic acid**

**Figure 3 (a) Strong polyelectrolyte, (b) Weak polyelectrolyte**

### 1.3.1 IMPORTANCE OF POLYELECTROLYTES

- Polyelectrolytes have a wide range of biological, industrial as well as fundamental applications. DNA, the carrier of genetic code, is a well known polyelectrolyte [3].

- In biological systems, binding of proteins and nucleic acids, functioning of enzymes and the construction of cellular components are controlled by tensions imposed by electrostatic interactions in polyelectrolytes [4].
- In biomedical field, they are widely used as dental adhesives, as control release devices in drug delivery, and biocompatible materials. In pharmaceuticals it is used for thickening syrups, and coating of tablets.
- Polyelectrolytes have wide range of industrial applications, in paints, as stabilizers, flocculants, and surface active agents in waste water treatment [5].
- They are also active ingredients in personal care products, and food industries.
- Polyelectrolytes have extensive applications in optoelectronic devices and nano-structured thin film coatings. The optoelectronics nano-thin film applications have been made possible by the fabrication of polyelectrolyte multilayers which involves sequential adsorption of positively and negatively charged polymers on to the surface of the substrate [6].

### 1.3.2 POLYELCTROLYTE CONFORMATION AND FACTORS AFFECTING IT

The electrostatic inetractions between the charged monomeric – monomeric units and monomeric units – counterions play a decisive role in the polyelectrolyte conformation. Due to the repulsive electrostatic inetractions between likely charged monomeric units polyelectrolyte chains assume an extended conformation. However the presence of excess counterions reduces the effective repulsive inetractions between the likely charged monomeric units. This decrease in the effective inetractions results the random coil conformation of the polyelectrolyte chains. The variation from the extended to random coil to globule conformation of polyelectrolytes also depends on various solution conditions which tend to modify the electrostatic interactions.

- Factors affecting Polyelectrolyte Conformation

The behaviour of polyelectrolyte is controlled by many parameters such as the ionic strength, solution pH, polyelectrolyte charge, concentration, solvent quality and temperature [7].

- Ionic strength: The charges on a linear polyelectrolyte chain will repel each other due to Columbic repulsion which causes the chain to adopt a more expanded, rigid rod – like conformation. But if salt concentration increases, the counter ions will screen the oppositely charged monomeric units and consequently polyelectrolyte chains will collapse to a more conventional random coil conformation.

- Solution pH: The polyelectrolyte chains will dissociate depending on the solution pH thus changing the number of charges on backbone. The resulting charge density will then decide the conformation of polyelectrolyte chains. This effect is more pronounced in case of weak polyelectrolyte [7].
- Polyelectrolyte concentration: On dissolving the polylectrolytes in a solvent at low concentrations they tend to acquire an extended conformation as whole of the solution volume is available to it. However with rise in polymer concentration the chains tend to fold onto themselves due to non – availability of the solution volume to the chains. This happens irrespective of the absence or physical presence of the neighbouring chains. This effect is known as the excluded volume effect.
- Solvent quality: Solvent quality is yet another deciding factor for the polyelectrolyte conformation. In a good solvent the solvent – polymer interaction is enhanced as compared to polymer – polymer interaction thus expanding the polymer chains. The reverse of this effect is seen in a poor solvent where the polymer – polymer interaction is greater and the chains remain in a coiled or globular state. For example proteins are denaturated when dissolved in guanidine HCl or urea.
- Temperature: The polyelectrolyte conformation is controlled by the temperature as well. On decreasing the temperature of a polymer solution at theta condition results in a globular conformation of the polyelctrolyte chains which is due to increased polymer – polymer interaction against the polymer – solvent interaction.

### 1.3.3 EFFECT OF SALTS ON POLYELCTROLYTE CONFORMATION

As stated above polyelectrolytes are the polymeric chains having ionizable groups in polar solvents, these groups dissociate into a charged polymer chain and small counterions. Usually due to the strong electrostatic repulsion between the uncompensated charges on the polymer it acquires an extended conformation. With the addition of salts this extended conformation changes to a coil like structure due to the screening of polyion charges. The extent of contraction depends on valency of dissociated ions and salt concentration[8].

When a monovalent salt like sodium chloride is added to a polyelectrolyte solution the dissociated $Na^+$ charges tend to screen oppositely charged polyions. Thus the effective electrostatic repulsion between the neighbouring ions will be reduced resulting in a coil conformation.

When divalent or trivalent salt is added, due to their higher valency they will attract more charges and the screening will be high as compared to monovalent ones. So the reduction in size of the chains in presence of multivalent salts will be occur at a very low concentration of salt as compared to monovalent salt [9].

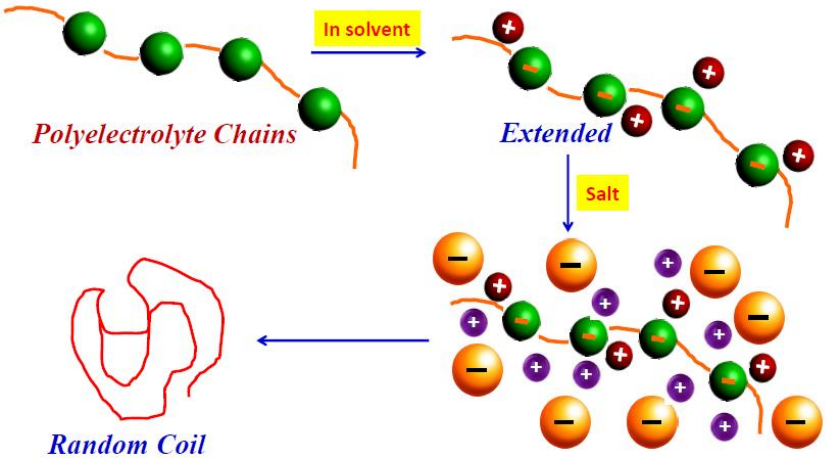



**Figure 4 Effect of ionic strength on the polyelectrolyte conformation**

- Importance of Conformational Studies

The properties of polyelectrolytes are determined not only by their primary chemical composition, but to a large degree by conformation of polymer chains.

The adsorption behavior of polyelectroltye mainly depends upon the state of conformation of the polymer chain. The conformation of polyelectrolyte helps them to "stick" to the solid substrate via intermolecular forces and charges created by the dissociation of various side groups. So due to this special characteristics polyelectrolytes are used extensively in layer – by – layer adsoption technique and the fabrication of nano – filteration membrane and many more.

# CHAPTER – 2
# LITERATURE SURVEY

Dubois and Boue studied the conformation of sodium and calcium salts of polystyrenesulfonic acid in presence of multivalent ions by small-angle neutron scattering (SANS). They studied the sodium salt of polystyrenesulfonic acid in presence of sodium ($Na^{+}$), calcium ($Ca^{+2}$) and lanthanum ($La^{+3}$) ions while the calcium salt of the acid was studied only in presence of calcium ions ($Ca^{+2}$). At lower ionic strength they did not observe any significant change in the polyelectrolytes chain conformation irrespective of the valency of the ions. However in presence of multivalent salts at highest concentration the chain appears thicker and ionic strength is no longer the controlling parameter. It may happen either due to the formation of bridging between monomers or by the influence of counter ions condensation [10].

Takahashi et al calculated the concentration dependence of radius of gyration $R_g$ of sodium polystyrenesulfonate (NaPSS) in aqueous solutions without added salt by using SANS over a wide range of concentration. The $R_g$ values obtained for the anionic NaPSS were always greater than the nonionic polystyerene chains, and in the concentrated region it is almost equal to that at theta condition [11].

Ahmad et al explained the effect of counter ion charge on viscosity of dilute polyelectrolyte solutions by using the Ostwald viscometer [12]. They varied the counter ion charge by adding the salts $NaCl, CaCl_2, AlCl_3$, For polystyrene sulfonate solutions without added salt the reduced viscosity increases with dilution, reaches to a maximum and then decreases in the limit of infinite dilution.

By using SANS Nierlich and his group studied polyelectrolyte solution in semi – dilute concentration regime in absence of any added salt. They found that both the persistence length $l_p$ and $q_m$, a factor which characterizes the interaction between the polymer chains, decrease with the increase in polyelectrolyte concentration [13].

Solis and co – worker used a theoretical model to study the structural transition of both single and double stranded DNA along with many other biological and synthetic polyelectrolytes by

increasing the concentration of multivalent salts [14]. They reported that at low monovalent salt concentration the expanded chains first collapsed into a neutral compact structure when the density of the multivalent salts approaches that of the monomer and with further increase in multivalent salt the chain re-dissolve acquiring an expanded coil conformation.

Fazli et al studied a model of rod like polyelectrolyte brushes in presence of both monovalent and multivalent counter ions and Monte Carlo simulation was used to study the solution without any added salt [15]. For a domain of grafting densities the brushes height is found to be relatively insensitive to the counter ions density and multivalent counter ions resulted in collapse of the brush in form of linked clusters.

Zhang and his co-partners used light scattering (LS) and atomic force microscopy (AFM) techniques for the conformational study of polyelectrolyte dendritic surfactant complexes in dilute solution of poly(diallydimethylammonium chloride) (PDADMAC). Three conformations one with a coil like structure and other two with polyelectrolyte behaviour were obtained from the data of SLS and DLS having almost same hydrodynamic radius. Some disordered globules formed by one or several coiled conformation of chains were noticed from AFM studies [16].

Wang and Yu studied the translational diffusion of sodium salts of poly(styrene sulfonate) (NaPSS) by dynamic light scattering as functions of salt concentration and molecular weight at a very low polymer concentration. They reported that with increasing salt density the hydrodynamic radius of NaPSS contracted from a size of $130$ Å $to$ $95$ Å. They observed that in $3.1$ $M$ KC1, NaPSS behaves like a neutral polymer with persistence length of $12$ Å in a $\theta$ solvent and in $0.15$ $M$ NaCl it behaves like a neutral polymer in good solvent [17].

Earnest and his co-workers studied the conformational behaviour of NaPSS by SANS by varying the polymer concentration over the range of $0 - 8.5$ $mol$ %. They found that the radius of gyration of NaPSS ionomers showed a regular increase with increasing sulfonate content but was insensitive towards the temperature variation above glass transition temperature [18].

Jia and Zhao studied the single chain conformation of a NaPSS during its re-entrant condensation by fluorescence correlation spectroscopy. The contraction and re-expansion of NaPSS chain were observed with the addition of counter ions of different ionic radius as well as valency [19].

# CHAPTER – 3
# EXPERIMENTAL TECHNIQUES

## 3.1 LOVIS MICROVISCOMETER

Viscosity measurements were carried out using microviscometer based on rolling ball principle. A ball rolls through a closed, sample filled capillary that is inclined at a defined angle and the inductive sensors determine the ball's rolling time between two graduated marks [20 – 21].

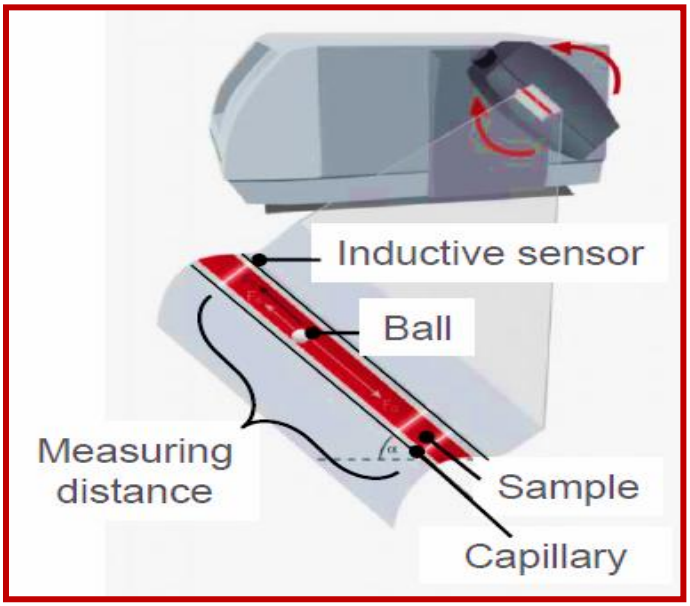



**Figure 5 Schematic diagram of rolling ball tube**

This measurement requires a very low sample volume ~ $100\mu L$ of sample. As it is seen from the figure when a steel ball rolls through transparent and opaque liquid kept inside a capillary, which moves in definite angle, then according to Hoeppler's falling ball principle, viscosity of the liquid modifies the velocity of the ball placed inside it. If the ball of volume $V$, radius $r$ and mass $m$ is used, then it is affected by a force acting downward given by the relation:

$$G = mg = V\rho_b g$$

where $\rho_b$ is the density of ball and $g$ is acceleration due to gravity. In an opposite direction, the ball is pulled up by the buoyant force $F_Z$, according to the Archimedes's principle. This force is equal to the weight of liquid displaced by the ball

$$F_Z = V\sigma g$$

Where $\sigma$ is the density of liquid. Finally, real liquid with dynamic viscosity $\eta$ generates a resistance against the movement of ball. This resistive force $F$ can be derived from the Stokes law given by:

$$F = 6\pi\eta r v$$

Where $v$ is the speed of ball. While the two previously mentioned forces ($G$ and $F_Z$) are static and do not depend on the speed $v$, the resistance $F$ increases with the speed. Thus, the speed of the falling ball will be increasing only until the net force is zero

$$G - F_Z - F = 0$$

From the combination of both the equations we got

$$V = \frac{2}{9} r^2 g \frac{\rho_b - \sigma}{\eta}$$

According to the above equation, the viscosity of liquid η can be determined from the runtime of the ball descending through this liquid as

$$\eta = K(\rho_b - \sigma)\,\Delta t$$

Where, $K$ is the proportionality constant, $\Delta t$ is the runtime of the measurement.

### 3.2 DYNAMIC LIGHT SCATTERING

Light being an electromagnetic wave an incident beam of light thus induces dipole in the molecules. This fluctuating dipole arises as the nuclei of the atoms and electrons experience an equal but opposite force. The induced dipoles then start oscillating with the same frequency as that of the incident beam. These fluctuating dipoles act as secondary sources of radiation which are better known as "scattered radiation". This is the basic reason why light gets scattered [22].

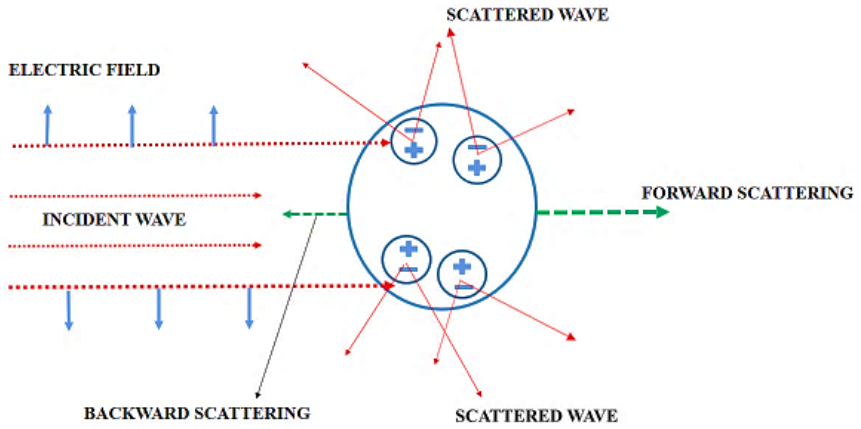



**Figure 6 Light scattering by an induced dipole moment due to an incident EM wave**

The intensity of the scattered light depends on the polarizability which further depends on the molecular weight [23] and can be expressed as:

$$\boldsymbol{\alpha = \frac{nM}{2\pi N_A}\left(\frac{dn}{dc}\right)}$$

Here $\alpha = polarizability$, $M = molecular\ mass$, $N_A = Avogadro's\ n$umber, $dn/dc = concentration\ dependence\ of\ refractive\ index$. Besides molecular weight dependence, light scattering also has a direct dependence on particle size.

Light scattering is basically of two types: static and dynamic depending on what parameters it measures. While static light scattering (SLS) measures the static properties like radius of gyration, molecular weight, second virial coefficient of the polymers the dynamic properties like diffusion coefficient and relaxation time is measured by dynamic light scattering (DLS). A major difference between SLS and DLS is the way light intensity is measured. SLS involves the measurement of average total intensity scattered light as a function of angle $\theta$. In contrast to this DLS measures the fluctuation in the scattered light.

In the present study we have used the dynamic light scattering to study the effect of multivalent salts on the conformation of NaPSS chains. DLS is a non – invasive and versatile technique to determine the relaxation time, diffusion coefficients and particle size of polymers. Light proves to be a suitable probe for the study of polymers as its wavelength is comparable with the size of the polymers which is of the order of few nanometers to few hundreds of nanometers.

As mentioned earlier that the incident beam induces dipoles in the molecules which fluctuates with the same frequency as that of the incident light. In solutions these molecules undergo Brownian motion due to constant collisions with the solvent molecules. Thus the fluctuating dipoles keep changing their positions constantly which results in fluctuations of scattered intensity with time.

Because of the Brownian motion the particles undergo frequent displacements from their positions and lead to slight variation in the frequency of scattered light as compared with the incident light. This is better known as the Doppler shift in the frequency. Because a slight

frequency (equivalent to energy) change is involved in DLS it is also known as the quasi – elastic light scattering (QELS). Dynamic light scattering measures these fluctuations in the scattered intensity with time which in turn is related to the particle size.

The figure below shows the Brownian motion of a molecule and how it leads to the fluctuations in the measured intensity.

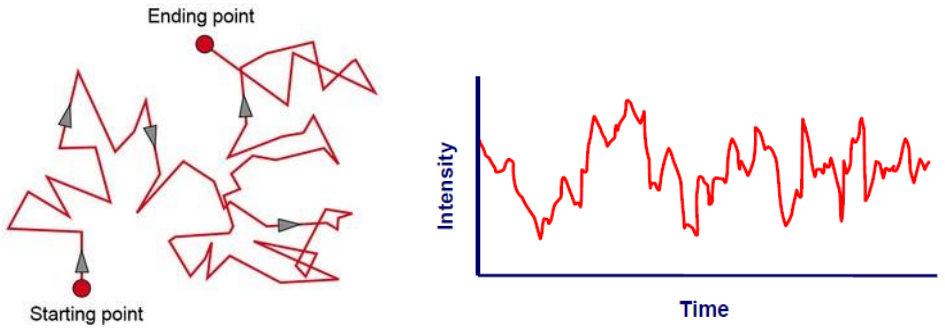



**Figure 7 Brownian motion of molecule and resulting intensity fluctuations**

The smaller particles move faster thus changing their positions more frequently as compared to larger particles hence their intensity fluctuates rapidly than the larger particles.

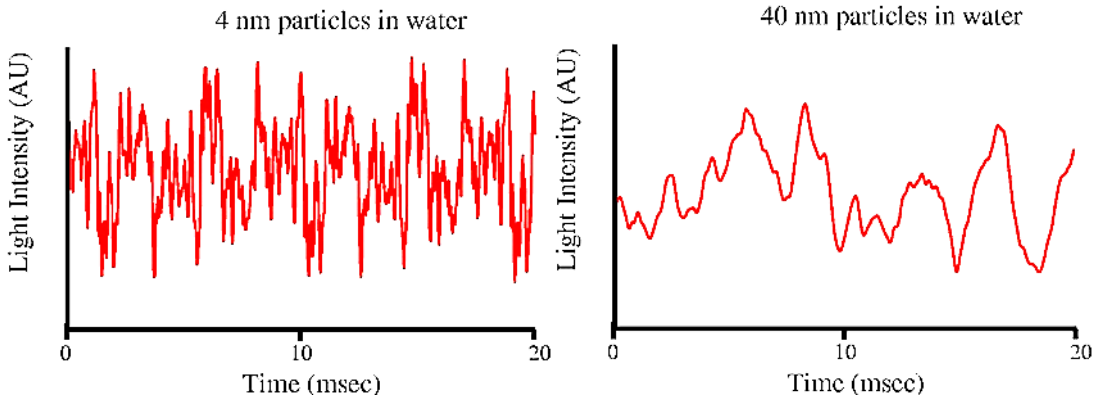



**Figure 8 Variation of intensity according to the particle size**

Thus particle size is the prime factor in deciding how well the intensity measured at time $'t'$ is correlated to the intensity measured at some later time $'t+\tau'$. This is the underlying principle of DLS which determines the physical parameters like relaxation time and diffusion coefficient [21].

The information on the particle dynamics is contained in the field – field autocorrelation function given by the relation:

$$g_1(q,\tau) = \frac{< E_S(t) E_S^*(t+\tau) >}{< |E_S(t)|^2 >}$$

However as all the detectors work on the principle of the square law, it is not possible to measure the electric field. Thus the experimentally measured quantity is the intensity and what we measure in DLS is the intensity – intensity autocorrelation from which the field – field autocorrelation can be extracted.

The intensity – intensity autocorrelation function is given by:

$$g_2(q,\tau) = \frac{< I_S(t) I_S^*(t+\tau) >}{< |I_S(t)|^2 >}$$

As stated earlier the intensity is measured at a time $'t'$ and at a later time $'t+\tau'$ we find that for small values of $'\tau'$the intensity is well correlated but after a long time there exist absolutely no correlation between the intensities as is evident from the figure.

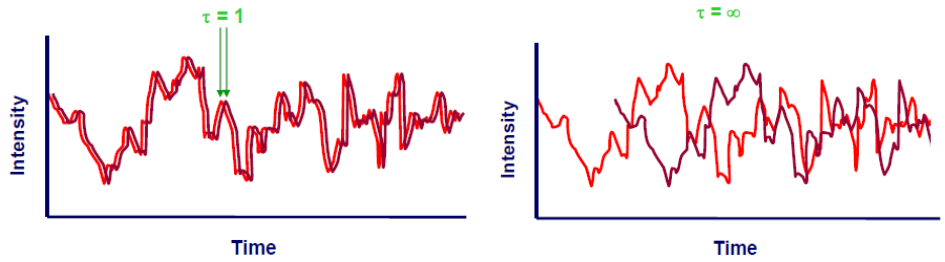



**Figure 9 Intensity correlations at short and long time intervals**

Therefore after a long time the intensity – intensity autocorrelation function tends to decay. From this intensity – intensity autocorrelation function the field – field autocorrelation function can be constructed using the Siegert's relation given by:

$$g_2(q,\tau) = 1 + \beta |g_1(q,\tau)|^2$$

where β is the coherence factor and whose value depends on the instrumental set – up. The field – field autocorrelation function is related to the decay constant $(\Gamma)$ by the relation

$$g_1(q,\tau) \sim \exp(-\Gamma\tau)$$

From the decay constant, the particle's diffusion coefficient $(D)$ can be calculated by using the relation:

$$\Gamma = Dq^2$$

Where, $q$ is the scattering vector given by $q = \frac{4\pi n}{\lambda_0} \sin\frac{\theta}{2}$

Where $n$ is the refractive index of the solution, $\theta$ is scattering angle, $\lambda_0$ is the wavelength of light in vacuum.

From the particles diffusion coefficient its size (or the hydrodynamic radius) can be estimated by using the Stokes – Einstein relation

$$D = \frac{k_B T}{6\pi\eta r_H}$$

where $k_B$ is the Boltzmann constant, $\eta$ is the viscosity of the solution and $r_H$ is the hydrodynamic radius of the particle. Thus the way the autocorrelation function decays reveals the dynamics of the system.

We used the dynamic light scattering set up of make Photocor as shown in the figure below. The experimental set up basically comprises of a light source (laser), thermostat, detector, signal amplifier and discriminator, and correlator. The schematic of a DLS set up is shown in the figure below.

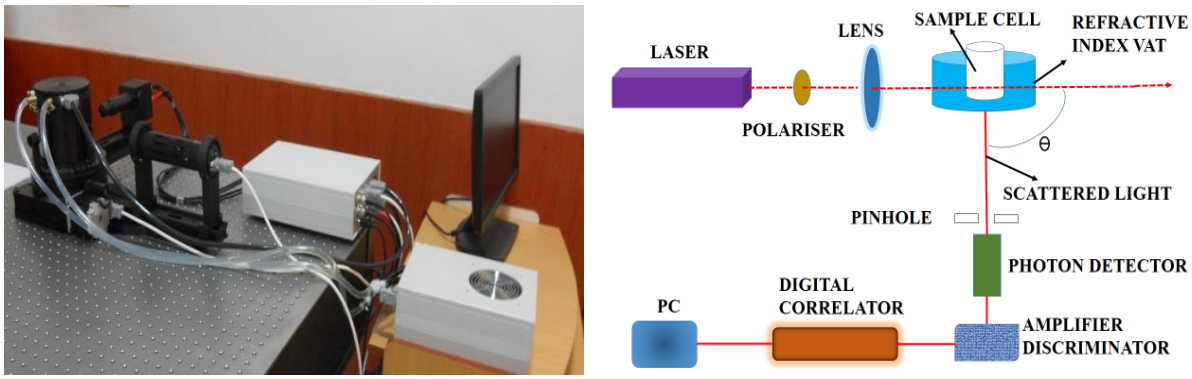



**Figure 10 Experimental set up and its Schematic diagram elucidating the major components**

# CHAPTER – 4
# SAMPLE SYNTHESIS

Light scattering technique is very sensitive to the quality of solution and the presence of small amount of dust or aggregates can strongly influence the observed data. The sample preparation is thus a tedious process when one wants to take light scattering data. We have taken sufficient precautions to avoid any type of contamination of our sample by dust or other foreign particles.
The sample cells and other glass wares used for sample preparation were first soaked in soap solution and washed with plain water. The cells and glass wares were then thoroughly rinsed and sonicated with doubly distilled water for about $20\ minutes$ at $40°C$ to remove any traces of soap solution. After sonication the cells were rinsed with clean acetone and left to dry. The cells were then thoroughly rinsed with Millipore water to remove traces of acetone. Before preparing sample the cells were however checked to reconfirm that they were clean by placing them in the laser beams path.

The required amount of Tris (tris[hydroxymethyl]aminomethane) was weighed and added to Millipore water. The pH of the Tris solution was adjusted by adding a few drops of hydrochloric acid. The pH of the resulting buffer solution of concentration $10mM$ was measured to be ~ 6.8. The buffer solution was then filtered using a $0.22\mu m$ membrane filter. All the samples were prepared in this filtered buffer solution.

Appropriate amount of sodium chloride was weighed and dissolved in the required amount of buffer solution to prepare $2M$ stock solution of sodium chloride. The salt was left overnight for proper dissolution of the salt. The salt solution was then centrifuged to remove any dust that might have gone into the solution during the process. Different concentrations ($500mM, 200mM, 100mM, 50mM, 10mM$ and $0M$) of salt solution was prepared by adding the appropriate amount of stock solution to required amount of buffer solution and were uniformly mixed by vortex mixer. The required amount of NaPSS was weighed and added to each of the salt solutions. The samples were left for about $5 - 6\ hours$ for proper dissolution of NaPSS in the salt solution. The prepared samples were then centrifuged for about $45\ minutes$ to remove any dust in it. After centrifuge the supernant was transferred to a clean and dry sample cell using

a micropipette. The entire sample preparation procedure was carried inside the horizontal laminar flow unit to avoid the contamination of samples by dust.

A part of the sample was taken for the viscosity measurements and rest was used for taking the light scattering data.

The flowchart below summarizes the above mentioned steps.

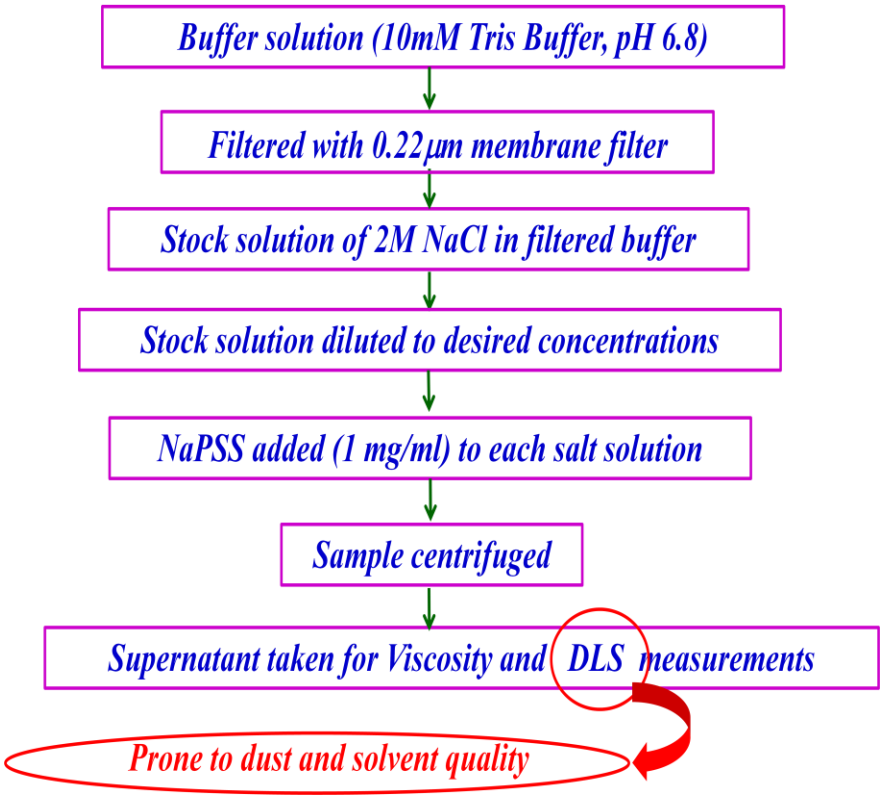



**Figure 11 Flowchart showing the sample preparation steps**

Similar steps were repeated for preparing the samples with varying concentrations of lanthanum chloride. However in case of lanthanum chloride ($LaCl_3$) we could not go beyond 1mM of $LaCl_3$ concentration because beyond this concentration the NaPSS did not dissolve properly and separated out from the solution. So we could only take measurements at lower concentration of $LaCl_3$ as compared to NaCl.

# CHAPTER – 5

# RESULTS AND DISCUSSIONS

## I. Viscosity Measurements

The solution viscosity ($\eta$) of sodium sulfonated polystyrene with different salts and at different salt concentration was measured using the LOVIS – Microviscometer. The samples were loaded into the capillary and placed in the capillary block and allowed to stand for ~ 5 – 10 min to attain the specified temperature. All the viscosity measurements were carried out at $25°C$. The capillary was thoroughly rinsed with Millipore water followed by ethanol to remove any traces of dust or other foreign particles. The capillary was allowed to dry before loading the fresh sample. The figure below shows the variation of solution viscosity with the rise in salt concentration.

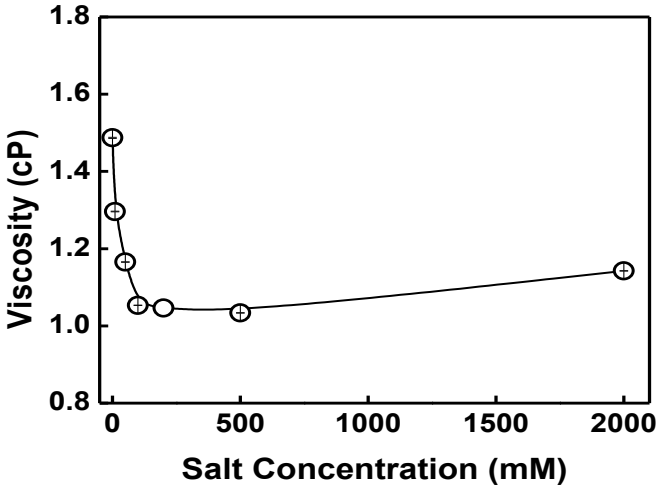



**Figure 12 Solution viscosity versus the NaCl concentration**

From the above figure it is observed that with the rise in salt concentration viscosity of NaPSS solution decreases. It can be explained in terms of the screening of the electrostatic interactions on the polymer chains. In presence of excess counter ions resulting from the dissociation of salt the charged monomeric units are effectively shielded from each other. It is because of this shielding that the extended polyelectrolyte chains tend to collapse giving rise to random coil conformation. The reduction of effective electrostatic interaction and collapse of polymer chains becomes apparent with decrease in solution viscosity.

The data obtained from viscosity measurements of NaPSS solutions in presence of sodium chloride is summarized in Table – I below.

**Table – I: Viscosity data of NaPSS solutions at different concentration of sodium chloride and lanthanum chloride salts**

| NaPSS concentration | NaCl Concentration (M) | $\eta_{NaCl}\ (cP)$ |
|---|---|---|
| $1mg/mL$ | 2 | $1.14 \pm 0.0005$ |
| | 0.5 | $1.03 \pm 0.0005$ |
| | 0.2 | $1.05 \pm 0.0000$ |
| | 0.1 | $1.05 \pm 0.0005$ |
| | 0.05 | $1.17 \pm 0.0005$ |
| | 0.01 | $1.30 \pm 0.0007$ |
| | 0 | $1.49 \pm 0.0014$ |

A similar decrease in solution viscosity was also observed on increasing the concentration of lanthanum chloride as is evident from the plot below.

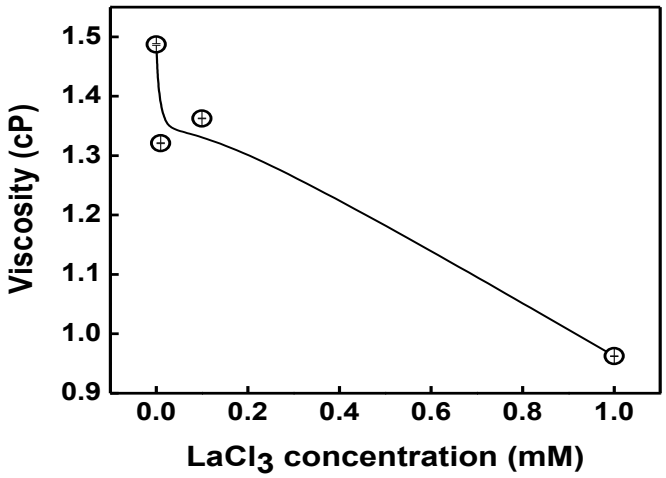



**Figure 13 Solution viscosity versus the NaCl concentration**

The viscosity data of NaPSS solutions with different amount of $LaCl_3$ has been summarized in Table II. A minimum of five runs was done to measure the viscosity of each of the NaPSS sample and the average of the runs was taken.

**Table – II: Viscosity data of NaPSS solutions at different concentration of lanthanum chloride ($LaCl_3$)**

| NaPSS concentration | $LaCl_3$ Concentration (mM) | $\eta_{LaCl_3}\ (cP)$ |
|---|---|---|
| $1mg/mL$ | 1 | $0.96 \pm 0.0005$ |
| | 0.1 | $1.36 \pm 0.0005$ |
| | 0.01 | $1.32 \pm 0.0005$ |

The viscosity of NaPSS solution without any added lanthanum chloride is same as above (1.49 ± 0.0014) cP and hence is not tabulated again. On comparing the viscosity data of solution it is found that the trivalent lanthanum ions screens polyion charges more effectively as compared to monovalent sodium ions. So even at very low concentrations of lanthanum ions a dramatic reduction of solution viscosity is observed. We could go only up to 1mM for lanthanum chloride as beyond this salt concentration the polymer separated out from the solvent. Studies show that this behavior of phase separation leading to formation of aggregates is seen in case of multivalent salts beyond certain salt concentration. However on increasing the salt concentration beyond another critical concentration the aggregates redissolve in the solvent forming a clear solution [19].

## II. Dynamic Light Scattering Measurements

The DLS measurements being highly prone to dust sufficient precautions were taken while preparing the samples for the same. The prepared samples were centrifuged to remove any signs of dust. The centrifuged samples were then transferred to clean and dry sample cell. The cell was then placed in the immersion cuvette and allowed for attaining the equilibrium temperature. All the measurements were carried out at $25°C$.

The autocorrelation function as obtained from the dynamic light scattering for NaPSS in $2M$ sodium chloride for one of the run and the corresponding particle size distribution is shown below.

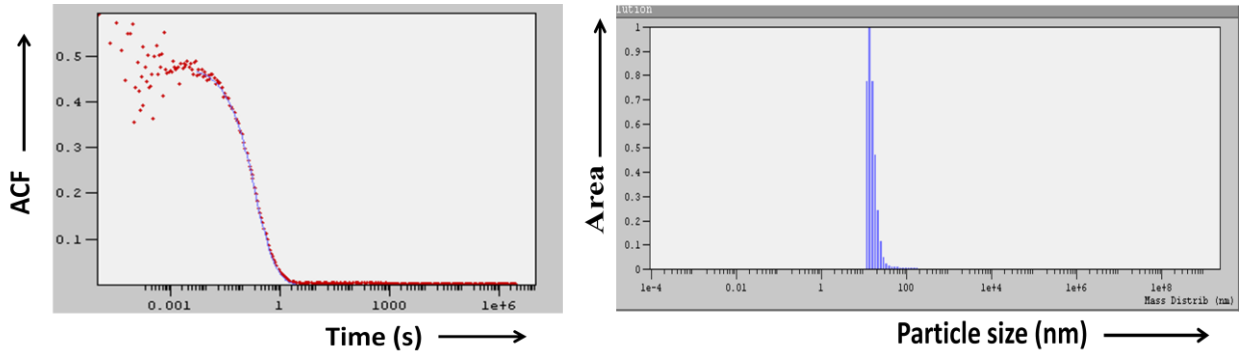



**Figure 14 Autocorrealtionfucntion and corresponding paticle size distribution as obatined from DLS for NaPSS in presence of 2M sodium chloride**

For each sample a minimum of six runs was done and the average value of the hydrodynamic radius (or particle size) obtained was taken. The average values of the hydrodynamic radius as

obtained for NaPSS at different concentrations of sodium chloride has been tabulated in Table – III.

**Table – III: Hydrodynamic radius of NaPSS in solution at different concentration of sodium chloride as measured by DLS**

| NaPSS concentration | NaCl Concentration (M) | $R_{H_{NaCl}}$ $(nm)$ |
|---|---|---|
| 1mg/mL | 2 | $15.7 \pm 4.20$ |
| | 0.5 | $26.3 \pm 1.00$ |
| | 0.2 | $27.3 \pm 1.26$ |
| | 0.1 | $41.7 \pm 1.86$ |
| | 0.05 | $46.3 \pm 4.54$ |

The average particle size so obtained from the DLS measurements was plotted against the corresponding salt concentration as shown below.

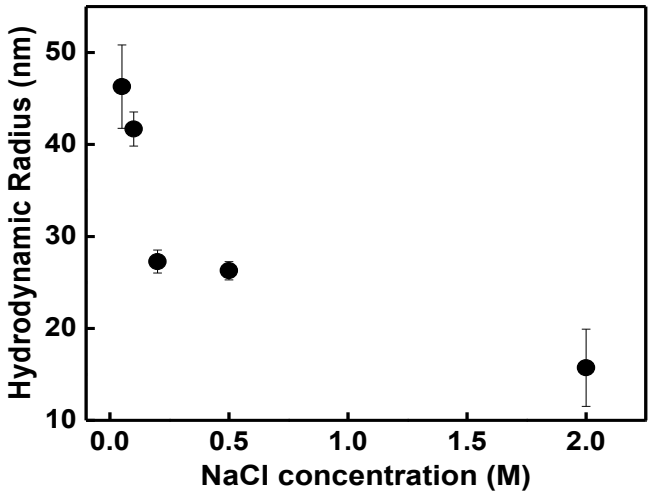



**Figure 15 Hydrodynamic radius versus the NaCl concentration**

The hydrodynamic radius (or particle size) exhibits a clear decrease with rise in concentration of sodium chloride. The decrease in particle size is yet another clear indication of the fact that chain folding of polyions occur due to the screening of its charges by counter ions.

As in case of sodium chloride the autocorrelation function and the particle size distribution of NaPSS in presence of lanthanum chloride is shown below. We obtained a smaller particle size ~ 8 $nm$ at a much lower salt concentration.

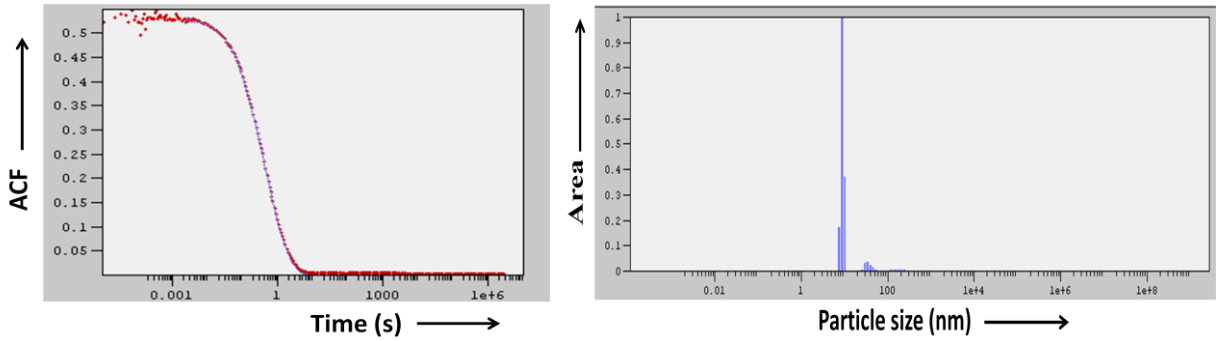



**Figure 16 Autocorrealtionfucntion and corresponding paticle size distribution as obatined from DLS for NaPSS in presence of 1mM lanthanum chloride**

Here also we did a minimum of six runs for each sample and the average value of the particle size was taken. The average value of particle size obtained at different concentrations of lanthanum chloride is tabulated in Table – IV.

**Table – IV: Hydrodynamic radius of NaPSS in solution at different concentration of lanthanum chloride as measured by DLS**

| NaPSS concentration | $LaCl_3$ concentration(mM) | $R_{H_{LaCl_3}}$ $(nm)$ |
|---|---|---|
| $1mg/mL$ | 1 | $7.4 \pm 1.55$ |
| | 0.1 | $9.3 \pm 2.49$ |
| | 0.01 | $17.6 \pm 2.22$ |

A similar decrease in the particle size was observed on increasing the lanthanum ion concentration as shown in the figure below. Here also we confined the concentration of lanthanum chloride to 1mM only so as to avoid any aggregate formation.

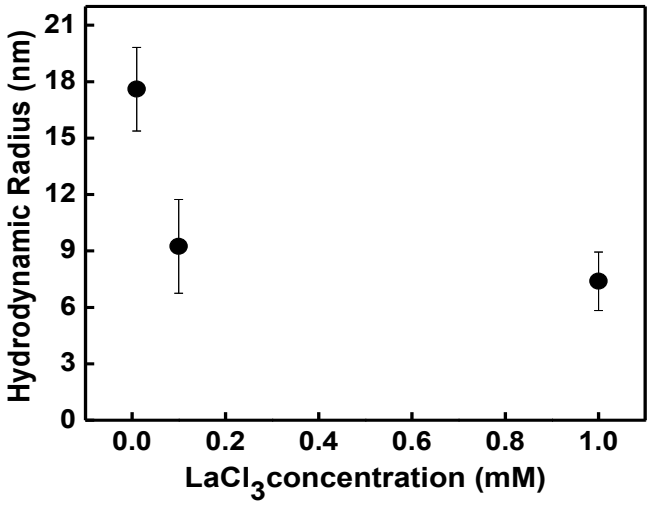



**Figure 17 Hydrodynamic radius versus the $LaCl_3$ concentration**

The results show that lanthanum ions have a striking effect on the decrease of particle size as compared to sodium ions. Unlike the sodium ions which are monovalent the lanthanum ions carry a net charge of +3. Moreover each monomeric unit of NaPSS carries a single charge on it. Thus the chains fold in a way to satisfy the valency of lanthanum ions as shown in the figure below. This folding leads to a more compact structure of polymer chains as compared to the structures formed in presence of sodium ions which carry a similar amount of charge as the monomeric units of the polyelectrolyte chains.

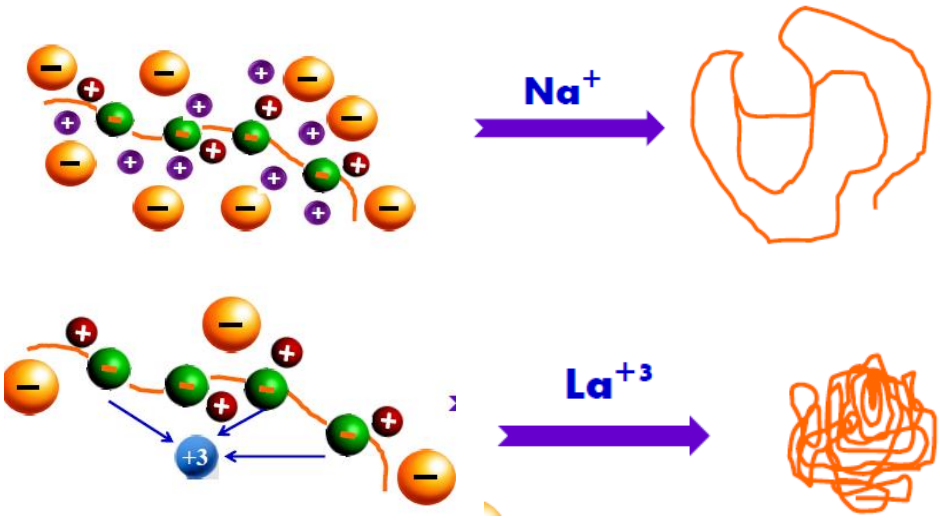



**Figure 18 Effective screening of polyion charges in presence of multivalent salts**

These observations indicate that the multivalent salts have a greater impact on the particle size as compared to the monovalent salts.

# CHAPTER – 6

# CONCLUSIONS

From our study we conclude that the presence of salts can effectively alter the electrostatic interactions between the polyions thus modifying the chain conformations. This change in conformation manifests itself in the viscosity changes. We found that with the rise in salt concentration the viscosity of NaPSS solutions decreased dramatically in both the cases of monovalent and trivalent ions. We also found that the hydrodynamic radius decreased with the rise in ionic strength. The trivalent ions had a conspicuous affect on the polyelectrolyte conformation as compared to the monovalent ions even at a low concentration.

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